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- **PATENT ABSTRACTS OF JAPAN vol. 018, no. 347 (C-1219), 30 June 1994 & JP 06 087765 A (AGENCY OF IND SCIENCE & TECHNOL;OTHERS: 01), 29 March 1994**

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Description

[0001] This invention relates to a process for separating a compound from a mixture of different compounds.

[0002] Processes for separating compounds from mixtures are of great importance, both in the laboratory and on an industrial scale. The purity of chemical compounds is dictated to a large extent by the purification step in which a compound is separated from other products of the reaction in which it is produced. The separation of a compound from its isomers, such as its regio and geometric isomers, can be particularly difficult to achieve. Conventional methods for separating a compound from its isomers include crystallisation and chromatography but these techniques can be relatively costly and time consuming and they do not always provide a sufficiently high degree of separation.

[0003] Layered double hydroxides are a class of compounds which comprise two metal cations and have a layered structure. A brief review of layered double hydroxides is provided in Chemistry in Britain, September 1997, pages 59 to 62. The hydrotalcites, perhaps the most well-known of the layered double hydroxides, have been studied for many years.

[0004] It is known that certain organic species may be intercalated into the layers in some layered double hydroxides and into clays. For Example, Ogawa et al., in Chemistry Letters, 1992, no. 3, p. 365-368, describe the intercalation of maleic and methylmaleic acids into the clay montmorillonite in a solid state reaction. The geometrical isomers of the acids, fumaric and methylfumaric acids, were not intercalated in the solid state reaction. However, when an ethanolic solution of the two isomers was used, the montmorillonite showed no selectivity and both isomers were intercalated.

[0005] The structure of the layered materials $[LiAl_2(OH)_6]X$, where X is Cl, Br or NO_3, and their hydrates has been described by Besserguenev et al., in Chem. Mater, 1997, no. 9, p. 241-247. The materials can be produced by the reaction of gibbsite [γ-$Al(OH)_3$] or other forms of $Al(OH)_3$, such as bayerite, nordstrandite or doyleite, with lithium salts of formula LiX. The materials can also be formed in other ways, such as by direct precipitation (see, for example, Serna et al, Clays & Clay Minerals, (1997), 25,384). The structure of the $LiAl_2(OH)_6^+$ layers in the compounds is unusual amongst layered double hydroxides since it is based on an ordered arrangement of metal cations within the layers.

[0006] The synthesis of $LiAl_2(OH)_6^+$ compounds is described in US 4348295 and US 4348297. The use of the materials for separating hydrocarbons and for gas chromatograph columns is taught in US 4430097 and US 4321065, respectively. In both of these latter two documents, the technology described does not involve intercalation chemistry but surface interactions with the stationary phase i.e., liquid-solid or gas-solid interactions.

[0007] Intercalates of compounds of formula $LiOH.2Al(OH)_3$ are described in US 4727167 and US 4812245. Both documents relate to uses of the intercalates as additives to organic materials such as mineral oils.

[0008] A few other layered double hydroxides having cation ordering are known. The layered double hydroxide $(Ca_2Al(OH)_6]_2{}^+SO_4{}^{2-}$ is an example.

[0009] Any improvement in the degree of selectivity or efficiency of a separation process can lead to increased purity of a product and, potentially, significant cost savings. The present invention provides a separation process which can be operated under very mild conditions and is highly selective. It also has the advantage of, in some cases, having a selectivity which is solvent and/or temperature dependent and can therefore be tuned towards a particular compound in a mixture. The process is based on the use of layered materials.

[0010] Accordingly, the present invention provides a process according to claim 1 for separating a compound from a mixture of different compounds.

[0011] The layered material used in the process of the present invention contains different cations within each layer in an ordered arrangement i.e., it has cation ordering. Ordered (i.e., non-random) arrangements of cations are believed to be a major factor in the selectivity of the process. The different types of cations may be cations of different metals or cations of the same metal having different oxidation states. Preferred layered materials are compounds containing layers of formula $LiAl_2(OH)_6^+$ or $Ca_2Al(OH)_6^+$ with the former being particularly preferred. However, other materials containing layers having cation ordering, such as other ordered layered double hydroxides, may be expected to be useful in the process of the invention.

[0012] The compound which is separated from the mixture by intercalation layered material is be readily recovered by treatment of the material with an anion which intercalates between the layers in the material in preference to the compound, thereby displacing the compound. Suitable anions for this purpose include inorganic anions such as carbonate and sulphate, for example, although anions which intercalate more or less strongly than carbonate can be used. Carbonate is preferred in most cases on account of its strong capacity for binding with the material which allows the guest (i.e., intercalated) compound to be recovered substantially quantitatively and since it potentially allows the material to be regenerated by calcining the carbonate intercalate and hydrating the resulting product. Typically, treatment of the material with carbonate to recover the compound may involve treating the material with an aqueous solution of a soluble carbonate salt (e.g., sodium carbonate) at about or above room temperature for up to several hours (e.g., at 20 to 80°C for from 1 to 20 hours).

[0013] The intercalated compound may also be separated from the layered material in other ways. For example, the material, with the compound intercalated, may be treated in such a way as to break down the material and thereby

free the compound (e.g., by treatment with a mineral acid). Alternatively, the intercalated compound may be removed by gradually protonating one or more of the negatively charged groups of the intercalated compound such that its retention within the material becomes energetically less favoured. Therefore, a further embodiment of the invention involves the recovery of the compound from the material by a method which comprises treatment with an acid under conditions which cause protonation and de-intercalation of the compound whilst leaving the layers of the material substantially intact.

[0014] The fact that the compound can be recovered from the material has clear advantages. Firstly, it allows the material to be regenerated, as mentioned above. Secondly, it means that a mixture of two compounds can be separated to provide each compound alone. For instance, a hypothetical mixture of A and B can be treated with the material to remove A from the mixture by intercalation into the material to leave behind B. The material with A intercalated is then removed from B, for example by filtration, and is treated with an anion, such as carbonate, to release A which can be readily separated from the carbonate intercalate of the material, for example by filtration. Alternatively, A could be released from its intercalate with the material by breaking down the material (e.g., by treatment with aqueous acid) and extraction of A into an organic solvent in a conventional biphasic extraction method.

[0015] The process of the invention involves the treatment with the layered material of a solution of the mixture containing the compound to be separated. Suitable solvents are those which dissolve the compound. The solvents may be aqueous or non-aqueous (e.g., polar, organic solvents such as THF or acetonitrile) but, when non-aqueous solvents are used, it is preferred that they are used as mixtures with water (e.g., THF containing 10% water). The nature of the solvent can be important to the selectivity of the process. For example, when the process is used to separate a mixture of isomers, it has been found that the nature of the solvent can affect which isomer is intercalated with one isomer intercalated in some solvents and another intercalated in others.

[0016] The temperature at which the process is carried out may also affect the selectivity of the process and it has surprisingly been found that different compounds may be preferentially intercalated from the same mixture at different temperatures. Preferably, the process is carried out at temperatures from 0°C up to the boiling point of the solvent, more preferably 20°C to 100°C. Temperatures of below 0°C may be employed with certain solvents having low freezing points, although the low rates of intercalation at the lower temperatures may not always provide a practically effective process.

[0017] The fact that the temperature and/or the solvent system used in the process can influence its selectivity can be used to target a particular compound for separation. Also, it means that the same material can be used to separate different compounds from the same mixture simply by varying the solvent and/or the temperature. Suitable temperatures and solvents for particular separations can be readily determined by routine experimentation in each case. Therefore, the process of the invention may involve selection of the solvent system and/or temperature so as to optimise the intercalation of the compound into the material.

[0018] The intercalation of the compound into the material can be complete in about 30 minutes to 2 hours at room temperature.

[0019] In order to effect intercalation, the solution of the mixture may be passed through the material. Conventional chromatographical and filtration techniques can be used for this purpose. For example, the layered material can be provided as a chromatographic column. The layered material may be used in the column as such or together with a support (e.g., the material embedded in resin beads). Addition of a mixture to the column leads to the elution of non-intercalated compound or compounds from the column with the intercalated compound retained. Eluting with an anion which intercalates in preference to the already intercalated compound de-intercalates the adsorbed compound. The column may then be reactivated (e.g., by calcination or, in the case of $[LiAl_2(OH)_6]^+$ layered materials, addition of concentrated LiCl solution or HCl solution). Alternatively, the mixture may be treated with the material in other ways such as, for example, by stirring a suspension of the material in the mixture.

[0020] The process of the invention can be used to separate a compound from one or more other structurally related or unrelated compounds having the same or different functional groups. The process of the invention has been found to be particularly suitable for the separation of a compound from a mixture of the compound and its isomers and this is, therefore, a preferred feature of the process. Preferably, the isomers are geometric isomers or regio-isomers. Mixtures of this type can be difficult to separate effectively using conventional methods. Alternatively, the isomers may be diastereoisomers or optical isomers; using materials having chiral structures, for example formed in the presence of a chiral guest template, it is possible to separate the different optical isomers of a compound. Layered materials suitable for separating optical isomers can be, for example, second stage intercalates (i.e., materials having intercalation in every other layer) which have chiral molecules (such as the anions of optically active diacids e.g., malic or tartaric acid) in every other layer; the optical isomers to be separated intercalate into the layers not already occupied by the chiral molecules.

[0021] The process of the invention may also be used in other separation processes, such as the separation of dianions from a mixture containing monoanions, for example. The dianions may be present as the minor or major component of the mixture.

[0022] The compounds intercalated into the material in the process of the invention comprise at least two negatively charged groups connected by a linker group. Since the compounds have at least two negatively charged groups (they may contain more than two negatively charged groups, but they preferably contain two), they are anionic although the anions may be formed solely for the purpose of the separation process. The negatively charged groups may be the anionic groups formed by the deprotonation of an acid, such as carboxylate (CO_2^-) and oxoanions of phosphorous and sulphur (e.g., phosphonate ($-PO_3^{2-}$), phosphate ($-OPO_3^{2-}$), sulphate ($-OSO_3^-$) and sulphonate ($-SO_3^-$)) or by the deprotonation of less acidic groups (e.g., alkoxide or phenolate) but are preferably carboxylate or sulphonate groups, more preferably carboxylate groups. The negatively charged groups in the compound may be the same or different. The linker group in the compounds provides connection between the negatively charged groups. The linker group may be wholly flexible (e.g., an alkylene chain) or it may have a degree of rigidity (e.g., an alkenylene chain). Preferably, the linker group provides a substantially rigid connection between the negatively charged groups to keep them at a substantially fixed distance apart. Suitable linker groups which provide a rigid connection include, for example, phenylene, naphthalene and other carbocyclic or heterocyclic, polyaromatic or non-aromatic, ring structures and 1,2-ethylene, each optionally substituted.

[0023] The process of the invention may be used to separate a wide variety of different types of compound including surfactants and biological molecules such as amino acids, sugars and polynucleotides, for example.

[0024] The process of the invention has been found to be particularly effective for the separation of the dianion of 1,4-benzenedicarboxylic acid from mixtures, for example mixtures comprising its 1,2- and 1,3- isomers and for the separation of the dianion of fumaric acid (i.e., trans-but-2-enedioic acid) from mixtures, for example mixtures comprising its cis-isomer, the dianion of maleic acid. The selectivity of materials containing layers having ordered cations in these separation processes is greater than 95% as determined by ^1H nmr. The separation of the 1,4- benzenedicarboxylic dianion from its isomers and the separation of maleate dianions from fumarate dianions are therefore preferred features of the process. The process of the invention thus enables the separation of the isomers of benzenedicarboxylic acids to be achieved, simply by forming the dianions from the acids by treatment with an alkali at a suitable pH for deprotonation of both of the acid groups. Similarly, fumaric and maleic acids may be separated by the process of the invention following the formation of their dianions in the same way. After the separation has been achieved, the acids may be reformed by protonation, for example using a mineral acid. Suitable water soluble benzenedicarboxylate, fumarate and maleate anions, which allow the process to be carried out in aqueous solution, are provided by the disodium salts.

[0025] The process is equally effective for other separations such as the separation of 1,5- and 2,6-naphthalenedisulphonates and 1,2- and 1,3-benzenedisulphonates, for example.

[0026] The material which is used in the process of the invention may be any substance which contains layers having at least two different cations within each layer with the cations ordered within the layers. The materials must, of course, be capable of intercalating the compound to be separated. Examples of suitable materials are compounds of formula $[LiAl_2(OH)_6]A$, having ordered $[LiAl_2(OH)_6]^+$ layers, wherein A is OH, F, Cl, Br, I, $(SO_4)_{½}$, or NO_3, optionally hydrated with stoichiometric or non-stoichiometric amounts of water, such as $[LiAl_2(OH)_6]Cl.H_2O$. The anion A is generally intercalated between the layers and must be capable of being displaced by the binding of the compound between the layers.

[0027] Without wishing to be bound by theory, it is believed that the selectivity of the layered materials may stem from the differing packing energies of the guest compounds within the interlayer region and their interactions with the positively charged, ordered layers. When benzenedicarboxylate dianions or mixtures of maleate and fumarate dianions are treated with $(LiAl_2(OH)_6]A$, for example, experimental results show that all of the anions are initially intercalated into the layers but that the layers subsequently contract to expel substantially all of the dianions except the favoured 1,4-benzenedicarboxylate and fumarate dianions.

[0028] Figures 1, 2 and 3 show, schematically, what is believed to be the mechanism underlying the separation process of the invention.

Figure 1 shows the steps leading to the intercalation of fumarate dianions from mixtures of these dianions with maleate dianions;

Figure 2 shows the intercalation of 1,4-dicarboxylate dianions from mixtures containing its 1,2- and 1,3- isomers; and

Figure 3 shows the displacement of 1,4-dicarboxylate dianions and fumarate dianions from their intercalates with the layered material using carbonate ions.

[0029] Referring to Figure 1, when $[LiAl_2(OH)_6]Cl.H_2O$ (1) is treated with equimolar mixtures of maleate and fumarate dianions, an increase in the layer spacing from 7.65 Å to 12.8 Å is initially observed, suggesting that all species are initially intercalated without significant selectivity. Layers (2) are of formula $[LiAl_2(OH)]_6^+$. The layer spacings then contract to 12.1 Å, as the energetically favoured fumarate dianions remain intercalated and their isomers leave the layers (2).

[0030] Similarly in Figure 2, when compound (1) is treated with equimolar mixtures of 1,2-, 1,3- and 1,4-benzenedicarboxylate dianions in aqueous solution, an increase in the layer spacing to 15.1 Å is initially observed with a subsequent contraction to 14.3 Å as the less favoured isomers leave the layers (2).

[0031] The effect of treating the 1,4-benzenedicarboxylate and fumarate intercalates with carbonate is shown, again schematically, in Figure 3. The dianions are released from between the layers in the material as carbonate ions are preferentially intercalated.

[0032] The layer spacings given in Figures 1, 2 and 3 were measured using X-ray diffraction techniques.

[0033] The process of the invention enables the separation of certain compounds having two negatively charged groups connected by a linker group with a high degree of selectivity, as measured by ^1H nmr, which may be greater than 95%, possibly greater than 98%. Thus, substantially quantitative separation may be achieved using the process of the invention, particularly if it is carried more than once on the same sample. The process may be used for the separation of a compound from mixtures in which it is present in from relatively small to relatively large amounts, e.g., for the isolation of small amounts of a compound from a mixture or for the removal of minor amounts of impurity from a compound.

[0034] The invention will now be described with reference to the following non-limiting examples.

EXAMPLES

A. $[LiAl_2(OH)_6]^+$ Compounds

Preparative Example $[LiAl_2(OH)_6]X.nH_2O$

[0035]

$$Al(OH)_3 + LiX \rightarrow [LiAl_2(OH)_6]X.nH_2O$$

[0036] $[LiAl_2(OH)_6]X.nH_2O$, where X is Cl, Br, OH or NO_3 and n is roughly equal to from 1 to 2, was prepared by stirring gibbsite ($Al(OH)_3$) in an aqueous solution of LiX at at least threefold molar excess at 90°C for 6 hours.

EXAMPLE 1

Separation of Fumarate and Maleate Isomers

[0037]

$$[LiAl_2(OH)_6]Cl.nH_2O + \underline{cis}\text{-}C_4H_2O_4 + \underline{trans}\text{-}C_4H_2O_4 \rightarrow$$

$$[LiAl_2(OH)_6)_2[\underline{trans}\text{-}C_4H_2O_4).nH_2O + \underline{cis}\text{-}C_4H_2O_4$$

$$[LiAl_2(OH)_6]_2[\underline{trans}\text{-}C_4H_2O_4].nH_2O + Na_2CO_3 \rightarrow (LiAl_2(OH)_6]_2CO_3.nH_2O$$

$$+ \underline{trans}\text{-}C_4H_2O_4$$

[0038] 250mg of $[LiAl_2(OH)_6]Cl.nH_2O$, where n is roughly equal to 1, were suspended in a 0.1M (for each isomer) aqueous equimolar solution of cis- and trans- sodium but-2-enedioate ($Na_2C_4H_2O_4$) and the suspension was stirred at room temperature for 1 hour. Complete reaction of the trans- isomer by intercalation into the material was indicated by the absence of any Bragg peaks from the host lattice in the X-ray diffraction patterns and of Cl in the elemental microanalysis.

[0039] The intercalated trans- dicarboxylate ions were extracted from the host lattice by suspending the $[LiAl_2/OH)_6]_2$ [trans-$C_4H_2O_4$].nH_2O in a 0.1 M aqueous solution of sodium carbonate and stirring at 80°C for 24 hours.

EXAMPLE 2

Separation of 1,2-, 1,3- and 1,4-Benzenedicarboxylate isomers

[0040]

$$[LiAl_2(OH)_6]Cl.nH_2O + 1,2\text{-}C_8H_4O_4 + 1,3\text{-}C_8H_4O_4 + 1,4\text{-}C_8H_4O_4 \rightarrow$$

$$[LiAl_2(OH)_6]_2[1,4\text{-}C_8H_4O_4].nH_2O + 1,2\text{-}C_8H_4O_4 + 1,3\text{-}C_8H_4O_4$$

$$[LiAl_2(OH)_6]_2[1,4\text{-}C_8H_4O_4].nH_2O + Na_2CO_3 \rightarrow [LiAl_2(OH)_6]_2CO_3.nH_2O + 1,4\text{-}C_8H_4O_4$$

[0041] 250mg of $[LiAl_2(OH)_6]Cl.nH_2O$ were suspended in a 0.1 M (for each isomer) aqueous equimolar solution of sodium 1,2-, 1,3- and 1,4-benzenedicarboxylate ($Na_2C_8H_4O_4$) and the mixture was stirred at room temperature for one hour. Complete intercalation of the 1,4-isomer into the material was indicated by the absence of any Bragg peaks from the host lattice in the X-ray diffraction patterns and of Cl in the elemental microanalysis.

[0042] The intercalated 1,4-benzenedicarboxylate ions were extracted from the host lattice by suspending the $[LiAl_2(OH)_6]_2[1,4\text{-}C_8H_4O_4].nH_2O$ in a 0.1 M aqueous solution of sodium carbonate and stirring at 80°C for 24 hours.

EXAMPLE 3

Separation of 1,5- and 2,6-Naphthalenedisulphonates

[0043]

$$[LiAl_2(OH)_6]Cl.nH_2O + 1,5\text{-}C_{10}H_6(SO_3)_2^{2-} + 2,6\text{-}C_{10}H_6(SO_3)_2^{2-}$$

$$\rightarrow [LiAl_2(OH)_6]_2[1,5\text{-}C_{10}H_6(SO_3)_2].nH_2O + 2,6\text{-}C_{10}H_6(SO_3)_2^{2-}$$

[0044] The procedure of Example 2 was repeated at 100°C using an equimolar mixture of 1,5- and 2,6- naphthalenedisulphonates in place of the benzenedicarboxylate mixture.

[0045] Resonances attributed to only the 1,5- isomer were seen in the ^1H-NMR spectrum of the intercalate and Bragg reflections corresponding to only the $1,5\text{-}C_{10}H_6(SO_3)_2^{2-}$ intercalate were observed in the XRD of the product. Thus, a selectivity for the separation of the 1,5- isomer of at least 99% can be inferred.

[0046] The selectivity decreased from 99% with decreasing temperature and there was found to be a change in the selectivity below about 40°C such that 73% of the intercalate formed at 20°C is the $2,6\text{-}C_{10}H_6(SO_3)_2^{2-}$ intercalate.

EXAMPLE 4

Separation of 1,2- and 1,3-Benzenedisulphonates

[0047]

$$[LiAl_2(OH)_6]Cl.nH_2O + 1,2\text{-}C_6H_4(SO_3)_2^{2-} + 1,3\text{-}C_6H_4(SO_3)_2^{2-}$$

$$\rightarrow [LiAl_2(OH)_6]_2[1,2\text{-}C_6H_4(SO_3)_2].nH_2O + 1,3\text{-}C_6H_4(SO_3)_2^{2-}$$

[0048] The procedure of Example 2 was repeated at various temperatures within the range 20 to 100°C using a mixture of 1,2- and $1,3\text{-}C_6H_4(SO_3)_2^{2-}$ in place of the benzenedicarboxylate mixture.

[0049] Intercalation was selective (99% or greater at all temperatures) for the 1,2- isomer; XRD patterns showed Bragg reflections characteristic of only the 1,2- isomer and ^1H-NMR resonances attributed to only 1,2- $C_6H_4(SO_3)_2^{2-}$ were observed.

EXAMPLE 5

Separation of 2,6-disubstituted Naphthalenes

[0050]

$$[LiAl_2(OH)_6]Cl.nH_2O + 2,6\text{-}C_{10}H_6(CO_2)_2^{2-} + 2,6\text{-}C_{10}H_6(SO_3)_2^{2-}$$

$$\rightarrow [LiAl_2(OH)_6]_2[2,6\text{-}C_{10}H_6(CO_2)_2].nH_2O + 2,6\text{-}C_{10}H_6(SO_3)_2^{2-}$$

[0051] The procedure of Example 2 was repeated using a mixture of $2,6\text{-}C_{10}H_6(CO_2)_2^{2-}$ and $2,6\text{-}C_{10}H_6(SO_3)_2^{2-}$ in place of the benzenedicarboxylate mixture.

[0052] Selective intercalation of $2,6\text{-}C_{10}H_6(CO_2)_2^{2-}$ was observed throughout the temperature range, increasing from 91% at 20°C to at least 99% at 100°C. Secondary exchange with Na_2CO_3 was found to be ineffective for this guest dianion so anion exchange reactions were carried out in D_2O. The percentage of the guest intercalation was then inferred by ^{1}H-NMR of the solution containing the dianions remaining after the intercalation reaction. Bragg reflections in the XRD pattern of the products do not correspond to the pure intercalate of either guest but correspond to a d-spacing between the two. This suggests an intermediate situation in which the same guest dianion is situated within a particular layer but the layers are randomly stacked with respect to each other.

EXAMPLE 6

Separation of 1, 2-disubstituted Benzenes

[0053]

$$[LiAl_2(OH)_6]Cl.nH_2O + 1,2\text{-}C_6H_4(SO_3)_2^{2-} + 1,2\text{-}C_6H_4(CO_2)_2^{2-}$$

$$\rightarrow [LiAl_2(OH)_6]_2[1,2\text{-}C_6H_4(CO_2)_2].nH_2O + 1,2\text{-}C_6H_4(SO_3)_2^{2-}$$

[0054] Example 5 was repeated using a mixture of $1,2\text{-}C_6H_4(SO_3)_2^{2-}$ and $1,2\text{-}C_6H_4(CO_2)_2^{2-}$.

[0055] The dicarboxylate was intercalated preferentially over the disulphonate with a temperature-independent selectivity of 70%, as determined by ^{1}H-NMR of the products.

EXAMPLE 7

Separation of 1,3-disubstituted Benzenes

[0056]

$$[LiAl_2(OH)_6]Cl.nH_2O + 1,3\text{-}C_6H_4(SO_3)_2^{2-} + 1,3\text{-}C_6H_4(CO_2)_2^{2-}$$

$$\rightarrow [LiAl_2(OH)_6]_2[1,3\text{-}C_6H_4(CO_2)_2].nH_2O + 1,3\text{-}C_6H_4(SO_3)_2^{2-}$$

[0057] Example 6 was repeated using a mixture of $1,3\text{-}C_6H_4(SO_3)_2^{2-}$ and $1,3\text{-}C_6H_4(CO_2)_2^{2-}$.

[0058] Again, the dicarboxylate was preferentially intercalated, this time with a temperature-independent selectivity of 90%, as determined by ^{1}H-NMR of the products.

EXAMPLES 8-18

Variation of Selectivity with Temperature and Solvent

[0059] Competitive intercalation reactions were run with equimolar amounts of two guests in the solution mixture. A 50% mixture of water and THF was used in Example 17. In all other cases, the solvent was water. 300 mg of host $[LiAl_2(OH)_6]Cl.nH_2O$ was stirred with an equimolar amount of each guest molecule, preserving a 2:1 guest excess.

Experimental conditions and results are summarised in the table below.

[0060] Secondary exchange was carried out on the intercalated solid with a three-fold excess of Na_2CO_3 (410 mg) in 5ml D_2O. This was stirred at 60°C for approximately 2 hours. The filtrate is retained and the residue washed in H_2O and EtOH. X ray diffraction was performed on the dry powder as a check that the original guest is fully exchanged with CO_3^{2-}. In cases where the guest did not fully exchange out, the reaction was repeated in the original D_2O solution. NMR was performed on the filtrates and the integrals measured to determine the ratio of intercalated molecules.

[0061] The 1,5-naphthalenedicarboxylic acid (Examples 8, 9, 17 and 18) makes up a special case due to its lack of solubility. A 0.1 molar solution of the potassium carboxylic acid salt was made up by stirring the acid into a 0.2 molar KOH solution. Again 300 mg of host was used, with 13 ml of the solution and 375 mg of the 2,6-naphthalenedicarboxylic potassium salt. The reaction was then carried out as outlined above.

EXAMPLE	GUESTS		REACTION CONDITIONS		% GUEST INTERCALATED	
	A	B	TEMP°C	TIME	A	B
8	1,5-naphthalenedisulfonate	2,6-naphthalenedisulfonate	0	6 days	48	52
			20	24h	27	73
			40	24h	52	48
			60	24h	73	27
			80	24h	79	21
			100	24h	98	2
9	-naphthalenesulfonate	1,5-naphthalenedisulfonate	20	24h	63	37
			60	24h	58	42
			100	24h	50	50
10	2-naphthalenesulfonate	2,6-naphthalenedisulfonate	20	24h	87	13
			60	24h	82	18
			100	24h	76	24
11	1,2-benzenesulfonate	1,3-benzenedisulfonate	20	2h	98	2
			60	2h	99	1
			100	2h	99	1
12	1,3-benzenedicarboxylate	1,4-benzenedicarboxylate	100	1h	3	97
13	1,2-benzenedicarboxylate	1,3-benzenedicarboxylate	20	1 h	92	8
			100	1h	90	10
14	2,6-naphthalenedicarboxylate	2.6-naphthalenedisulfonate	20	24h	91	9
			60	24h	99	1
			100	24h	99	1
15	1,2-benzenedicarboxylate	1,2-benzenedisulfonate	20	2h	68	32
			60	2h	67	33
			100	2h	71	29
16	1,3-benzenedicarboxylate	1,3-benzenedisulfonate	20	2h	91	9

(continued)

EXAMPLE	GUESTS		REACTION CONDITIONS		% GUEST INTERCALATED	
	A	B	TEMP°C	TIME	A	B
			60	2h	92	8
			100	2h	91	9
17	1,5-naphthalenesulfonate (50%THF)	2,6-naphthalenesulfonate	20	24h	53	47
			75	24h	62	38
18	1,5-naphthalenedicarboxylate	2,6-naphthalenedicarboxylate	20	24h	10	90
			60	24h	3	97
			100	24h	<1	>99

[0062] Examples 8 to 18 demonstrate how the selectivity of the process of the invention varies with temperature and solvent and illustrate the tunability of the process to particular compounds. It will be appreciated that where the selectivity is relatively low, an effective separation can be obtained by multiple treatments of the mixture with the layered material.

EXAMPLES 19-23

Variation of Selectivity with Temperature and Solvent Polarity

[0063] Competitive intercalation reactions using equimolar mixtures of 1,5-naphthalenedisulphonate and 2,6-naphthalenedisulphonate and the host $[LiA_2(OH)_6]Cl.nH_2O$ were performed as previously described. A variety of other solvent systems were tried. 50:50 mixtures of water and another polar organic solvent were used as they could dissolve the di-sodium salts of the naphthalenedisulphonate anions.

EXAMPLE	SOLVENT	GUESTS		REACTION CONDITIONS		% GUEST INTERCALATED	
		A	B	TEMP°C	TIME	A	B
19	water	1,5-naphthalenedisulphonate^{2-}	2,6-naphthalenedisulphonate^{2-}	20 60 100	24 h 24 h 24h	30 45 93	70 55 7
20	50% THF 50% water	1,5-naphthalenedisulphonate^{2-}	2,6-naphthalenedisulphonate^{2-}	20 75	24h 24h	53 62	47 38
21	50% ethanol 50% water	1,5-naphthalenedisulphonate^{2-}	2,6-naphthalenedisulphonate^{2-}	20 100	24h 24h	85 82	15 18
22	50% acetone 50% water	1,5-naphthalenedisulphonate^{2-}	2,6-naphthalenedisulphonate^{2-}	20 100	24h 24h	80 >99	10 <1
23	50% acetonitrile 50% water	1,5-naphthatenedisulphonate^{2-}	2,6-naphthalenedisulphonate^{2-}	20 100	24h	83 90	17 10

EXAMPLE 24

Method for recovering the organic guest anions from the host lattice and recovering the ion exchange capacity for the host lattice.

[0064] 150mg of $[LiAl_2(OH)_6]_2[1,4\text{-}C_8H_4O_4].nH_2O$ was suspended in 5ml of 0.5M HCl(aq) in ethanol. The mixture was stirred at room temperature for 12 hours. X-Ray diffraction of the resulting solid showed that it had been largely converted to $[LiAl_2(OH)_6]Cl.H_2O$ with a small amount of the 2nd stage intercalation compound $[LiAl_2(OH)_6][1,4\text{-}C_8H_4O_4][Cl).nH_2O$ also present.

[0065] Repetition of the experiment described above using 1.0M HCl(aq) in ethanol lead to the compete replacement of $1,4\text{-}C_8H_4O_4$ and the conversion of the solid to $[LiAl_2(OH)_6]Cl.nH_2O$ which can be used in future experiments.

[0066] The key feature of this process is that it provides an energy efficient, low temperature method for recovering the intercalated ions and simultaneously regenerating the host lattice.

B. $Ca_2Al(OH)_6^+$ Compounds

Preparative Example

[0067]

$$CaINO_3)_2.2H_2O + Al(NO_3)_3.9H_2O + NaOH + NaNO_3 \rightarrow [Ca_2Al(OH)_6]NO_3.$$

$$nH_2O \text{ (n approx. 2)}$$

[0068] $Ca(NO_3)_2.2H_2O$ and $Al(NO_3)_3.9H_2O$ were mixed together in water and the solution was added drop wise to a solution of NaOH and $NaNO_3$. The resulting precipitate was stirred at 60°C for 3 days. $[Ca_2Al(OH)_6)NO_3.nH_2O$ was characterised by X-ray powder diffraction and elemental microanalysis.

EXAMPLE 25

Separation of Fumarate and Maleate Isomers

[0069]

$$[Ca_2Al(OH)_6]NO_3.nH_2O + Na_2,\ \underline{cis}\text{-}C_4H_2O_4 + Na_2\ \underline{trans}\text{-}C_4H_2O_4 \rightarrow$$

$$[Ca_2Al(OH)_6]_2[\underline{cis}\text{-}C_4H_2O_4].nH_2O + [Ca_2AHOH)_6]_2[\underline{trans}\text{-}$$

$$C_4H_2O_4].nH_2O + NaNO_3$$

[0070] 200mg of $[Ca_2Al(OH)_6]NO_3.nH_2O$ was stirred in 5ml of water over a period of 24 hours with a 2-fold excess of an equimolar mixture of cis and trans di-sodium but-2-enedioate (sodium maleate and fumarate respectively). The reaction was carried out at room temperature (20°C) and 100°C to see the effects of temperature on the selectivity of the process.

[0071] The degree of selectivity of the ion-exchange intercalation in crystalline $[Ca_2Al(OH)_6]NO_3.nH_2O$ was determined by recovering the organic guest ions by ion-exchange with CO_3^{2-} ions according to the equation:

$$[Ca_2Al(OH)_6]_2[\underline{cis}\text{-}C_4H_2O_4].nH_2O + [Ca_2Al(OH)_6]_2[trans\text{-}$$

$$C_4H_2O_4].nH_2O + Na_2CO_3 \rightarrow$$

$$[Ca_2Al(OH)_6]_2CO_3.nH_2O + Na_2\ \underline{trans}\text{-}C_4H_2O_4 \text{ and } Na_2\ \underline{cis}\text{-}C_4H_2O_4$$

[0072] The procedure was as follows: The isolated intercalate produced in the reaction described above was stirred with a 3 fold excess of Na_2CO_3 in 5ml of D_2O at 50 °C overnight. The solid was collected by filtration, washed with

water and checked by X-ray diffraction to see if all the original organic guests had been exchanged out of the solid. The solution was retained and studied by 1 H NMR to determine the ratio of anions present.

GUESTS		REACTION CONDITIONS		% GUEST INTERCALATED	
A	B	TEMP°C	TIME	A	B
cis-$C_4H_2O^{2-}$	trans-$C_4H_2O_4^{2-}$	20	24 h	< 1	> 99
cis-$C_4H_2O_4^{2-}$	trans-$C_4H_2O_4^{2-}$	100	24h	83	17
Note: In contrast to the results observed here, the other host $[LiAl_2(OH)_6]Cl.nH_2O$ shows no temperature dependent intercalation for cis versus trans-$C_4H_2O_4^{2-}$ in water. At 100°C in water the intercalation preferences are also reversed between the two host materials.					

Claims

1. A process for separating a compound from a mixture of different compounds, the compound to be separated comprising at least two negatively charged groups connected by a linker group which process comprises:

(A) providing a solution comprising a solvent in which the mixture of different compounds is dissolved,
(B) treating the solution with a layered material comprising layers containing at least two different types of cation disposed in an ordered arrangement within each layer of the layered material to selectively intercalate the compound to be separated between the layers in the layered material and separate it from the dissolved mixture,
(C) removing the layered material containing the intercalated compound from the solution; and
(D) treating the layered material containing the intercalated compound to recover the compound.

2. A process according to claim 1, wherein the layered material comprises layers of formula $[LiAl_2(OH)_6]^+$ or $[Ca_2Al(OH)_6]^+$.

3. A process according to either claim 1 or claim 2, wherein in step (D) the compound is recovered from the layered material by treatment of the layered material with an anion which intercalates into the layered material in preference to the compound.

4. A process according to claim 3, wherein the anion is carbonate.

5. A process according to either claim 1 or claim 2, wherein in step (D) the compound is recovered from the layered material by a method which comprises treatment with an acid under conditions which cause protonation and deintercalation of the compound whilst leaving the layers of the layered material substantially intact.

6. A process according to any one of claims 1 to 5, wherein the mixture of different compounds comprises a compound comprising at least two negatively charged groups connected by a linker group and isomers thereof and wherein the compound is separated from its isomers.

7. A process according to claim 6, wherein the isomers are geometric or regio- isomers.

8. A process according to any one of claims 1 to 5, wherein the compound is a dianion and the mixture comprises one or more monoanions.

9. A process according to any one of claims 1 to 8, wherein the solution of the mixture is passed through the layered material.

10. A process according to any one of claims 1 to 9, wherein the solvent in which the mixture is dissolved is selected so as to optimise the intercalation of the compound into the material.

11. A process according to any one of claims 1 to 10, wherein the linker group is phenylene, 1,2-ethylene or naphthalene, each optionally substituted.

12. A process according to any one of claims 1 to 11, wherein the negatively charged groups are carboxylate or sulphonate groups.

13. A process according to claim 12, wherein the compound is the dianion of 1,4-benzenedicarboxylic acid and the mixture comprises the dianions of 1,2-benzenedicarboxylic acid and/or 1,3-benzenedicarboxylic acid.

14. A process according to claim 12, wherein the compound is the dianion of fumaric acid and the mixture comprises the dianion of maleic acid.

15. A process according to either 13 or claim 14, wherein the dianion is prepared by deprotonation of the corresponding dicarboxylic acid.

16. A process according to any one of claims 13 to 15, wherein the compound is the dianion of a disodium salt or dipotassium salt.

17. A process according to any one of claims 13 to 16, wherein the separated compound is protonated to form the corresponding dicarboxylic acid.

18. A process according to any one of claims 1 to 17, wherein the temperature at which the solution of the mixture is treated with the layered material is selected so as to optimise the intercalation of the compound into the layered material.

Patentansprüche

1. Verfahren zur Abtrennung einer Verbindung aus einer Mischung verschiedener Verbindungen, wobei die abzutrennende Verbindung wenigstens zwei über eine Verbindungsgruppe verbundene negativ geladene Gruppen enthält, wobei man bei dem Verfahren:

   (A) eine Lösung bereitstellt, die ein Lösungsmittel enthält, in dem die Mischung der verschiedenen Verbindungen gelöst ist,
   (B) die Lösung mit einem geschichteten Material behandelt, das Schichten enthält, die in jeder Schicht des geschichteten Materials mindestens zwei verschiedene, in einem geordneten System befindliche Kationen enthält, um die abzutrennende Verbindung selektiv zwischen den Schichten im geschichteten Material zu interkalieren und sie von der gelösten Mischung abzutrennen,
   (C) das die interkalierte Verbindung enthaltende geschichtete Material aus der Lösung entfernt, und
   (D) das die interkalierte Verbindung enthaltende geschichtete Material zur Rückgewinnung der Verbindung behandelt.

2. Verfahren nach Anspruch 1, wobei das geschichtete Material Schichten der Formel $[LiAl_2(OH)_6]^+$ oder $[Ca_2Al(OH)_6]^+$ enthält.

3. Verfahren nach Anspruch 1 oder 2, wobei in Schritt (D) die Verbindung aus dem geschichteten Material zurückgewonnen wird, indem man das geschichtete Material mit einem Anion behandelt, das besser als die Verbindung in das geschichtete Material interkaliert.

4. Verfahren nach Anspruch 3, wobei es sich bei dem Anion um Carbonat handelt.

5. Verfahren nach Anspruch 1 oder 2, wobei man in Schritt (D) die Verbindung durch ein Verfahren, bei dem man mit einer Säure unter Bedingungen behandelt, die zur Protonierung und Deinterkalierung der Verbindung führen, wobei die Schichten des geschichteten Materials im wesentlichen intakt bleiben, aus dem geschichteten Material zurückgewinnt.

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei die Mischung der verschiedenen Verbindungen eine Verbindung enthält, die wenigstens zwei durch eine Verbindungsgruppe verbundene negativ geladene Gruppen enthält, sowie Isomere davon, und wobei die Verbindung von ihren Isomeren abgetrennt wird.

7. Verfahren nach Anspruch 6, wobei es sich bei den Isomeren um geometrische Isomere oder Regioisomere handelt.

8. Verfahren nach einem der Ansprüche 1 bis 5, wobei es sich bei der Verbindung um ein Dianion handelt und die Mischung ein oder mehrere Monoanionen enthält.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei die Lösung der Mischung durch das geschichtete Material geleitet wird.

10. Verfahren nach einem der Ansprüche 1 bis 9, wobei das Lösungsmittel, in dem die Mischung gelöst ist, so ausgewählt ist, daß die Interkalierung der Verbindung in das Material optimiert ist.

11. Verfahren nach einem der Ansprüche 1 bis 10, wobei es sich bei der Verbindungsgruppe um Phenylen, 1,2-Ethylen oder Naphthalin handelt, jeweils gegebenenfalls substituiert.

12. Verfahren nach einem der Ansprüche 1 bis 11, wobei es sich bei den negativ geladenen Gruppen um Carboxylat- oder Sulphonatgruppen handelt.

13. Verfahren nach Anspruch 12, wobei es sich bei der Verbindung um das Dianion von 1,4-Benzoldicarbonsäure handelt und die Mischung die Dianionen von 1,2-Benzoldicarbonsäure und/oder 1,3-Benzoldicarbonsäure enthält.

14. Verfahren nach Anspruch 12, wobei es sich bei der Verbindung um das Dianion von Fumarsäure handelt und die Mischung das Dianion von Maleinsäure enthält.

15. Verfahren nach Anspruch 13 oder 14, wobei das Dianion durch Deprotonierung der entsprechenden Dicarbonsäure hergestellt wird.

16. Verfahren nach einem der Ansprüche 13 bis 15, wobei es sich bei der Verbindung um das Dianion eines Dinatriumsalzes oder Dikaliumsalzes handelt.

17. Verfahren nach einem der Ansprüche 13 bis 16, wobei die abgetrennte Verbindung zur Bildung der entsprechenden Dicarbonsäure protoniert wird.

18. Verfahren nach einem der Ansprüche 1 bis 17, wobei die Temperatur, bei der die Lösung der Mischung mit dem geschichteten Material behandelt wird, so ausgewählt ist, daß die Interkalierung der Verbindung in das geschichtete Material optimiert ist.

Revendications

1. Procédé pour séparer un composé d'un mélange constitué de différents composés, le composé à séparer comprenant au moins deux groupements chargés négativement liés par un groupement de liaison, lequel procédé comprend ;

   (A) la mise en oeuvre d'une solution comprenant un solvant dans lequel est dissous le mélange des différents composés,
   (B) le traitement de la solution avec un matériau multicouches comprenant des couches qui comprennent au moins deux types différents de cations disposés en agencement ordonné dans chaque couche du matériau multicouches afin d'intercaler de manière sélective le composé à séparer entre les couches du matériau multicouches et à le séparer du mélange dissous,
   (C) l'enlèvement de la solution du matériau multicouches comprenant le composé intercalé ; et
   (D) le traitement du matériau multicouches comprenant le composé intercalé afin de récupérer le composé.

2. Procédé selon la revendication 1, **caractérisé en ce que** le matériau multicouches comprend des couches de formule $[LiAl_2(OH)_6]^+$ ou $[Ca_2Al(OH)_6]^+$.

3. Procédé selon la revendication 1 ou la revendication 2, **caractérisé en ce que**, dans l'étape (D), le composé est récupéré à partir du matériau multicouches par traitement du matériau multicouches avec un anion qui s'intercale dans le matériau multicouches préférentiellement par rapport au composé.

4. Procédé selon la revendication 3, **caractérisé en ce que** l'anion est le carbonate.

5. Procédé selon la revendication 1 ou la revendication 2, **caractérisé en ce que**, dans l'étape (D), le composé est récupéré à partir du matériau multicouches par un procédé qui comprend le traitement avec un acide dans des conditions provoquant la protonation et la désintercalation du composé tout en laissant les couches du matériau multicouches essentiellement intactes.

6. Procédé selon l'une quelconque des revendications 1 à 5, **caractérisé en ce que** le mélange des différents composés comprend un composé comprenant au moins deux groupements chargés négativement liés par un groupement de liaison et des isomères de celui-ci, et **en ce que** le composé est séparé de ses isomères.

7. Procédé selon la revendication 6, **caractérisé en ce que** les isomères sont géométriques ou sont des régioisomères.

8. Procédé selon l'une quelconque des revendications 1 à 5, **caractérisé en ce que** le composé est un dianion et le mélange comprend un ou plusieurs monoanions.

9. Procédé selon l'une quelconque des revendications 1 à 8, **caractérisé en ce que** l'on fait passer la solution du mélange à travers le matériau multicouches.

10. Procédé selon l'une quelconque des revendications 1 à 9, **caractérisé en ce que** le solvant dans lequel le mélange est dissous est choisi de manière à optimiser l'intercalation du composé dans le matériau.

11. Procédé selon l'une quelconque des revendications 1 à 10, **caractérisé en ce que** le groupement de liaison est le phénylène, le 1,2-éthylène ou le naphtalène, chacun étant facultativement substitué.

12. Procédé selon l'une quelconque des revendications 1 à 11, **caractérisé en ce que** les groupements chargés négativement sont des groupements carboxylate ou sulfonate.

13. Procédé selon la revendication 12, **caractérisé en ce que** le composé est le dianion de l'acide 1,4-benzènedicarboxylique et le mélange comprend les dianions de l'acide 1,2-benzènedicarboxylique et/ou de l'acide 1,3-benzènedicarboxylique.

14. Procédé selon la revendication 12, **caractérisé en ce que** le composé est le dianion de l'acide fumarique et le mélange comprend le dianion de l'acide maléique.

15. Procédé selon la revendication 13 ou la revendication 14, **caractérisé en ce que** le dianion est préparé par déprotonation de l'acide dicarboxylique correspondant.

16. Procédé selon l'une quelconque des revendications 13 à 15, **caractérisé en ce que** le composé est le dianion d'un sel disodique ou d'un sel dipotassique.

17. Procédé selon l'un quelconque des revendications 13 à 16, **caractérisé en ce que** le composé séparé est protoné pour former l'acide dicarboxylique correspondant.

18. Procédé selon l'une quelconque des revendications 1 à 17, **caractérisé en ce que** la température à laquelle la solution du mélange est traitée avec le matériau multicouches est choisie de manière à optimiser l'intercalation du composé dans le matériau multicouches.

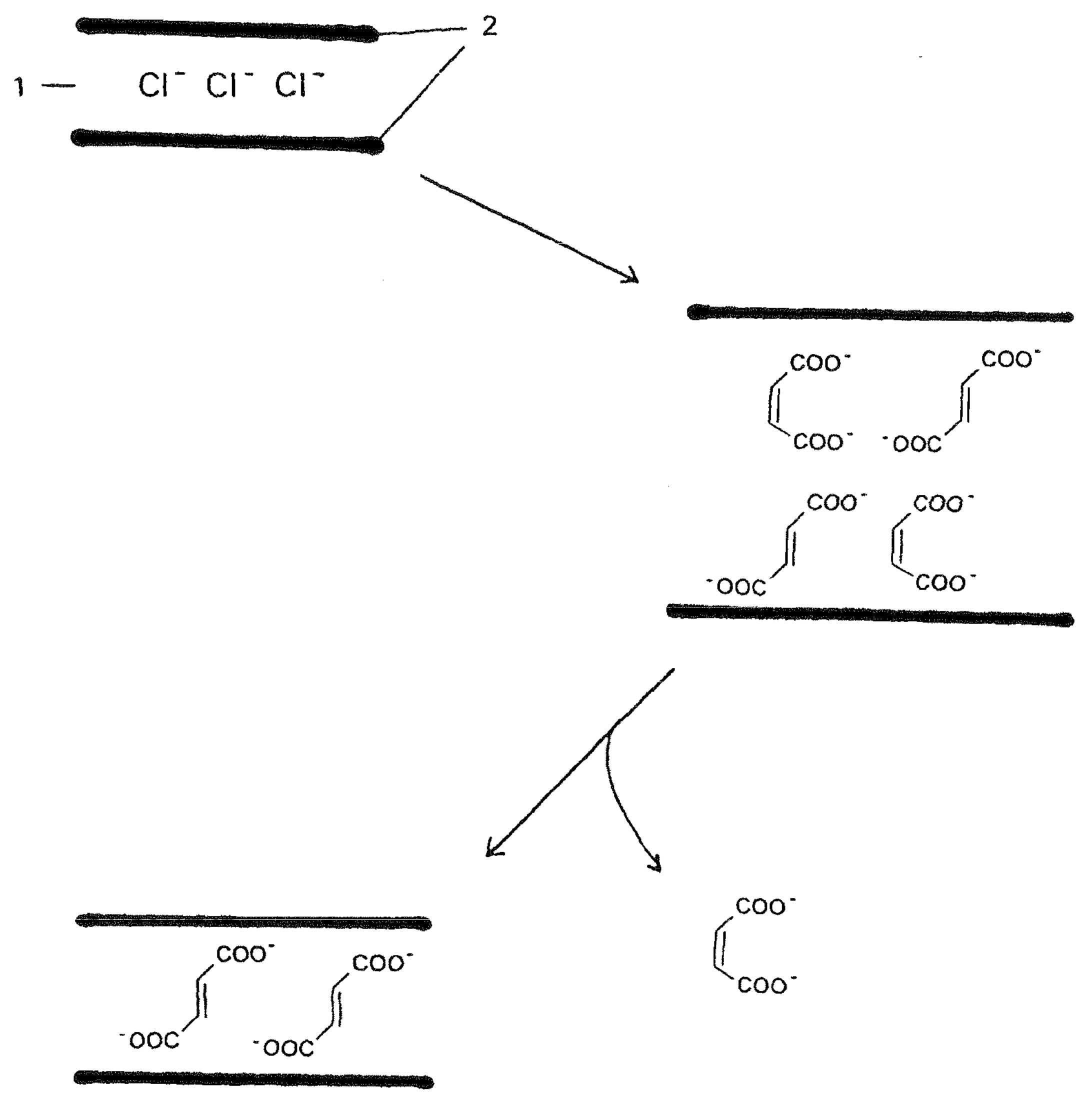

Figure 1

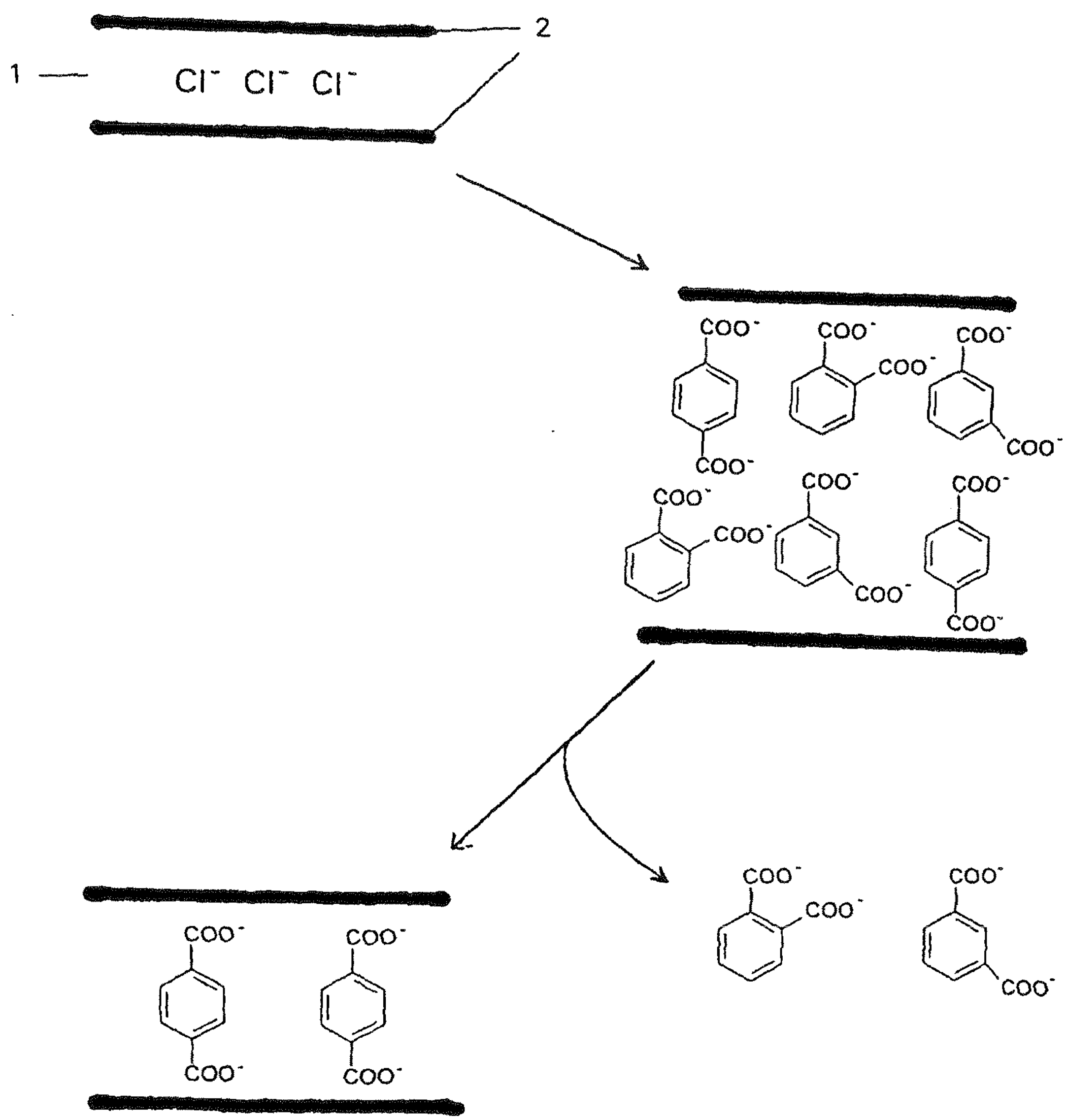

Figure 2

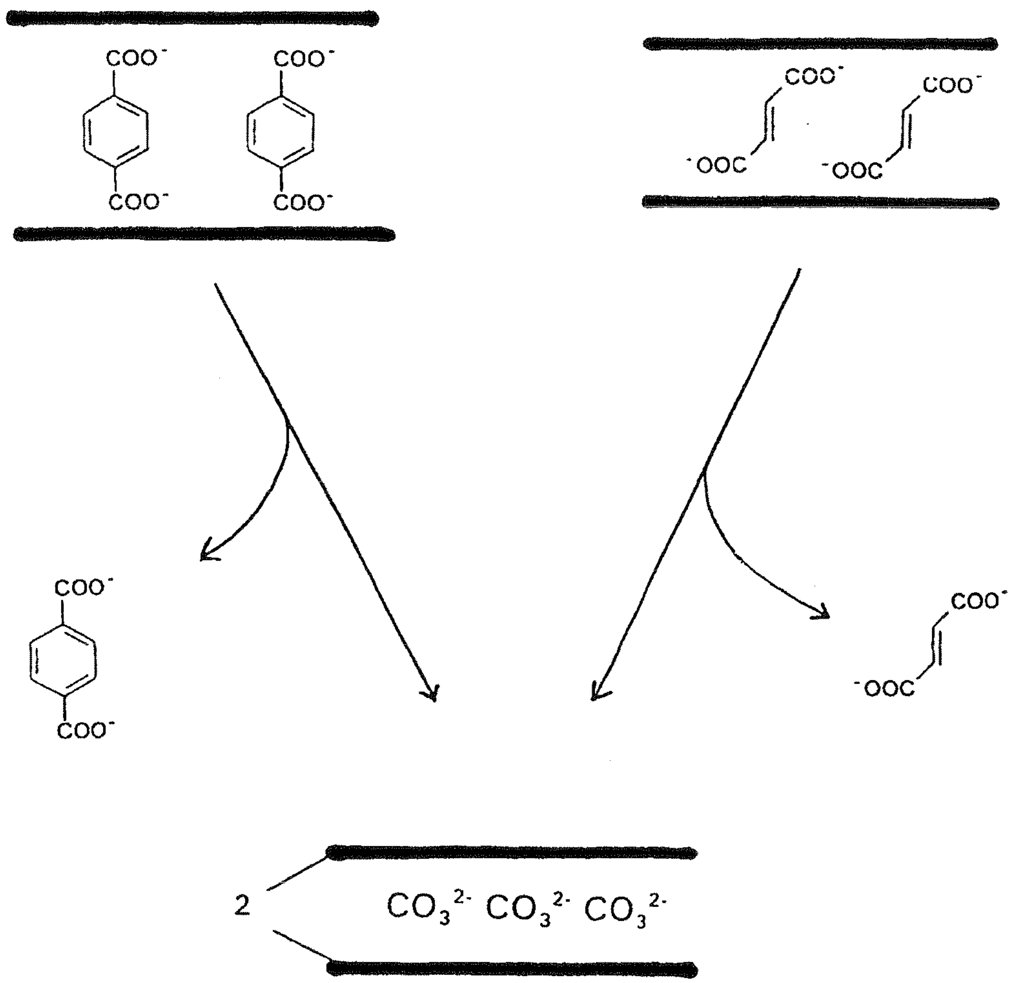

Figure 3